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(54) Title: SYNTACTIC POLYOLEFIN COMPOSITION FOR PIPE COATING

(57) Abstract: The invention relates to a syntactic polyolefin composition for pipe coating, wherein the composition comprises a β-nucleated propylene polymer and microspheres. The invention also relates to a method for the preparation of the composition for pipe coating and to an off-shore pipe coated with the syntactic polyolefin composition.

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SYNTACTIC POLYOLEFIN COMPOSITION FOR PIPE COATING

Field of the invention

The present invention relates to a syntactic poly-
olefin composition for pipe coating, to a method for the
preparation thereof and to an off-shore pipe coated with
5   the syntactic polyolefin composition.
Background of the invention

Polyolefin coated pipes are used in off-shore
applications for the transportation of hot fluids, e. g.
crude oil, and are often installed at the sea-bottom,
10   most often at depths of several hundred meters. For these
applications steel pipes are preferred but also fibre
reinforced pipes, advanced multilayer pipe constructions
made of metal and/or polymer based layers, may be used.
At these depths the temperature of the surrounding water
15   is close to 0°C which leads to extensive heat losses from
the transported fluid and significantly reduces flow or
causes blockage of the production lines. In order to
efficiently pump, e. g. crude oil, it is required that
the viscosity is sufficiently low, otherwise a higher
20   pump efficiency or the installation of additional heating
units along the pipeline will be necessary.

To meet the insulation requirements on off-shore
pipes it has previously been suggested to coat the pipes
with an insulating layer of so called syntactic polyole-
25   fins, i. e. composite polyolefin/filler materials in
which the filler comprises hollow microspheres. As exam-
ples of the polyolefin used mention may be made of e. g.
linear low density polyethylene, blends of propylene
polymers and olefin copolymer elastomers or syntactic
30   polypropylene.

A disadvantage of such syntactic polyolefin coatings
is the insufficient mechanical properties of pipes provi-
ded with such coatings. At the depths in question the

temperature difference between the surrounding water, often having a temperature as low as 0°C, and the inside of pipe, often having a temperature of 100-150°C, put high demands on the mechanical properties. The water

5 pressure on the coating is substantial, and without sufficient compression strength the insulating coating will be compressed to a smaller thickness, thereby reducing its insulating capacity. Also, excellent mechanical properties are required for coated pipes in order to avoid

10 cracking of the coating during installation handling and in service.

The term installation handling used herein means any installation technique such as coiling and uncoiling of the ready made pipelines, welding and other jointing

15 techniques and on-shore or off-shore installation, e. g. off-shore installation at the sea-bottom. Installation of coated pipes, in particular for off-shore applications, involves tough conditions for the protective coating layer, including high stress, substantial elongation,

20 surface damages, notches, impact events, etc, both at low and high temperature conditions and at high hydrostatic pressure. The coating layer is not only protecting the pipeline as such, but is also doing so in a state of high stress and/or at elevated temperatures and pressures,

25 making the coating most sensitive to cracking, e. g. the stresses induced during coiling and uncoiling. During the service life of the coated pipeline, the coating has to protect the pipeline from damages and induced stress and crack formations at conditions close to 0°C, high hydro-

30 static pressures where a small damage or notch in the coating could propagate into a large crack putting the pipeline as such at risk. With a high dynamic fracture toughness of the coating material no cracks will occur during installation handling and in service.

35 Another problem is the difficulties in producing syntactic polyolefins. In particular, it is difficult to compound glass microspheres and other hollow spherical

fillers into a thermoplastic polymer matrix at low enough shear forces to avoid crushing of the spheres during the process. Also, the thermal conductivity of an effective off-shore pipe insulation needs to be low. When about 15%

5   or more of the spheres in the matrix are crushed, it is difficult to maintain the necessary low level of thermal conductivity. Furthermore, the structural properties of the syntactic polyolefin are also adversely affected. This problem cannot be avoided by adding a larger amount

10   of microspheres since an excessive amount will cause additionally crushed microspheres due to higher forces involved during homogenisation, i. e. > 15%, initiates cracks and further deteriorates the mechanical proper-ties.

15   European Patent Application no EP-A-473 215 dis-closes polyolefin syntactic foams for pipeline insulation use, wherein microspheres that have been treated with a chain scission agent are added to a fluid stream of short chain polypropylene or polybutylene to form a syntactic

20   foam insulative material. This method is taught as useful for producing material of a low thermal conductivity. However, the plastic starting materials taught for use therein are generally not optimal for submarine pipe insulation, because while the short chain polypropylene

25   or polybutylene affords low breakage of the microspheres, the method requires the presence of a chain scission agent, coated on the microspheres. The chain-scission agent is employed to cause a narrowing of the molecular weight distribution of the polyolefin. Without the pres-

30   ence of this agent, the finished insulation would be unacceptable for use as off-shore pipe insulation, be-cause it would not be hydrostatic pressure resistant, abuse resistant, or creep resistant.

Summary of the invention

35   The object of the invention is to provide a syntac-tic polyolefin composition for pipe coating wherein the

above mentioned drawbacks have been eliminated or alle-
viated.

5   Thus, it is an object of the present invention to
provide a syntactic polyolefin composition having supe-
rior thermal and mechanical properties which may be pre-
pared on a large scale on currently available equipment.

According to the present invention this object is
achieved by a syntactic polyolefin composition for pipe
coating, characterised in that the composition comprises
10   a β-nucleated propylene polymer and microspheres, said
composition having a melt flow rate (MFR$_2$; ISO 1133, con-
dition D) at 230°C/2.16 kg in the range of 0.05-30 g/10
min and in that the composition has an elongation at
break of at least 3%.

15   A further object of the present invention is to pro-
vide a method for the preparation of a syntactic polyole-
fin composition for pipe coating, characterised in that
microspheres are evenly distributed by melt mixing in a
composition comprising a β-nucleated propylene polymer
20   and hollow microspheres, said composition having a melt
flow rate at 230°C/2.16 kg in the range of 0.05-30 g/10
min and in that the composition has an elongation at
break of at least 3%.

Yet another object of the present invention is to
25   provide an off-shore pipe coated with a syntactic poly-
olefin composition, characterised in that it is coated
with a composition according to any one of claims 1-13.

By the syntactic polyolefin composition of the pre-
sent invention it is possible to achieve a pipe coating
30   for off-shore installations having low thermal conductiv-
ity and excellent mechanical properties.

Other distinguishing features and advantages of the
invention will appear from the following specification
and the appended claims.

35   Detailed description of preferred embodiments

A characterising feature of the composition of the
present invention is the presence of a β-nucleated pro-

pylene polymer. β-nucleated propylene polymers are iso-
tactic propylene polymers composed of chains in a 3_1 heli-
cal conformation having an internal microstructure of β-
form spherulites being composed of radial arrays of par-
5   allel stacked lamellae. This microstructure can be real-
ized by the addition of β-nucleating agents to the melt
and subsequent crystallization. The presence of the β-
form can be detected through the use of wide angle X-ray
diffraction (Moore, J., Polypropylene Handbook, p 134-
10   135, Hanser Publishers Munich, 1996).

        In a preferred embodiment of the present invention
the β-nucleated propylene polymer is a (co)polymer (i. e.
a homopolymer or copolymer), characterised in that the β-
nucleated propylene polymer is a (co)polymer which comp-
15   rises at least 90.0 weight% of propylene and up to 10.0
weight% of α-olefins with 2 or 4 to 18 carbon atoms, and
that the propylene polymer has a melt flow rate of 0.1-8
g/10 min at 230°C/2.16 kg.

        According to a more preferred embodiment of the pre-
20   sent invention the β-nucleated propylene polymer is a β-
nucleated propylene block copolymer with 90.0 to 99.9
weight% of propylene and 0.1 to 10.0 weight % of α-ole-
fins with 2 or 4 to 18 carbon atoms with a melt flow rate
(MFR) of 0.1 to 40 g/10 min at 230°C/2.16 kg, preferably
25   0.1 to 8 g/10 min at 230°C/2.16 kg, whereby a test poly-
olefin pipe prepared from the β-nucleated propylene co-
polymer has a critical pressure of > 25 bars and a
dynamic fracture toughness of > 3.5 $MNm^{-3/2}$ in the hydro-
static small scale steady state (hydrostatic S_4) test at
30   3°C.

        The method of determining the dynamic fracture
toughness is disclosed in Plastics, Rubber and Composites
Processing and Applications, Vol. 26, No. 9, pp. 387 ff.

        According to another advantageous embodiment, the β-
35   nucleated propylene polymer is a β-nucleated propylene
block copolymer having an IR_τ > 0.98, a tensile modulus of
≥ 1100 MPa at 23°C and a Charpy impact strength, notched,

●

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of $\geq$ 6kJ/m^2 at -20°C. The IR$_\tau$ of the propylene polymer is measured by Infrared spectroscopy and calculated as described in EP 0 277 514 A2, page 3.

The β-nucleated propylene polymer in the composition
5 according to the present invention preferably has a melt flow rate of 0.1-70 g/10 min, more preferably 0.15-50 g/10 min, and most preferably 0.2-30 g/10 min at 230°C/2.16 kg.

According to a further preferred embodiment the β-
10 nucleated propylene polymer has a tensile modulus of preferably $\geq$ 1300 MPa and most preferably $\geq$ 1500 MPa at 23°C.

Charpy impact strength of the β-nucleated propylene polymer is preferably $\geq$ 6kJ/m^2 at -20°C, more preferably $\geq$
15 9kJ/m^2 at -20°C, most preferably $\geq$ 10 kJ/m^2 at -20°C.

According to a further embodiment, the β-nucleated propylene polymers are propylene copolymers obtained by polymerization with a Ziegler-Natta catalyst system comprising titanium-containing solid components, an organo-
20 alumina, magnesium or titanium compound as cocatalyst and an external donor according to the formula

$R_xR'_ySi(MeO)_{4-x-y}$,
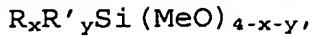
wherein R and R' are identical or different and are branched or cyclic aliphatic or aromatic hydrocarbon resi-
25 dues, and y and x independently from each other are 0 or 1, provided that x + y are 1 or 2.

A preferred external donor in the Ziegler-Natta catalyst system for producing the β-nucleated propylene block copolymers is dicyclopentyldimethoxysilane.

30 According to an advantageous embodiment the β-nucleated propylene copolymers contain 0,0001 to 2,0 wt%, based on the propylene copolymers used, of
– dicarboxylic acid derivative type diamide compounds
   from C_5-C_8-cycloalkyl monoamines or C_6-C_{12}-aromatic mono-
35   amines and C_5-C_8-aliphatic, C_5-C_8-cycloaliphatic or C_6-
   C_{12}-aromatic dicarboxylic acids, and/or

- diamine derivative type diamide compounds from C_5-C_8-cycloalkyl monocarboxylic acids or C_6-C_{12}-aromatic mono-carboxylic acids and C_5-C_8-cycloaliphatic or C_6-C_{12} aromatic diamines, and/or
- amino acid derivative type diamide compounds from amidation reaction of C_5-C_8-alkyl-, C_5-C_8-cycloalkyl- or C_6-C_{12}-arylamino acids, C_5-C_8-alkyl-, C_5-C_8-cycloalkyl- or C_6-C_{12}-aromatic monocarboxylic acid chlorides and C_5-C_8-alkyl-, C_5-C_8-cycloalkyl- or C_6-C_{12}-aromatic mono-amines, and/or
- quinacridone derivative compounds of the type quinacridone compounds, quinacridone-quinone compounds, and/or dihydroquinacridone type compounds, and/or
- dicarboxylic acid salts of metals from group IIa of periodic system and/or mixtures of dicarboxylic acids and metals from group IIa of periodic system, and/or
- salts of metals from group IIa of periodic system and imido acids of the formula

$$HOOC-[\!-CH_2-\!]_x-\underset{R}{\underset{|}{CH}}-N{\overset{\diagup CO}{\underset{\diagdown CO}{\diagdown}}}Y$$
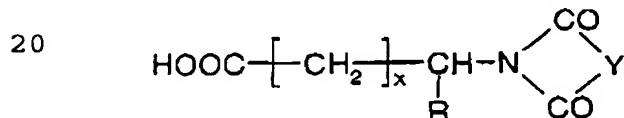
wherein x = 1 to 4; R = H, -COOH, C_1-C_{12}-alkyl, C_5-C_8-cycloalkyl or C_6-C_{12}-aryl, and Y = C_1-C_{12}-alkyl, C_5-C_8-cycloalkyl or C_6-C_{12}-aryl - substituted bivalent C_6-C_{12}-aromatic residues,

as β-nucleating agent.

Examples of the dicarboxylic acid derivative type diamide compounds from C_5-C_8-cycloalkyl monoamines or C_6-C_{12}-aromatic monoamines and C_5-C_8-aliphatic, C_5-C_8-cycloaliphatic dicarboxylic acids, optionally contained in the β-nucleated propylene copolymer, are

- N,N'-di-C_5-C_8-cycloalkyl - 2,6-naphtalene dicarboxamide compounds such as

N,N'-dicyclohexyl-2,6-naphtalene dicarboxamide and N,N'-dicyclooctyl-2-6-naphtalene dicarboxamide,

- N,N'-di-C$_5$-C$_8$-cycloalkyl-4,4-biphenyldicarboxamide com-
  pounds such as
  N,N'-dicyclohexyl-4,4-biphenyldicarboxamide and
  N,N'-dicyclopentyl-4,4-biphenyldicarboxamide,
5 - N,N'-di-C$_5$-C$_8$-cycloalkyl-terephthalamide compounds such
  as
  N,N'-dicyclohexylterephtalamide and
  N,N'-dicyclopentylterephtalamide,
- N,N'-di-C$_5$-C$_8$-cycloalkyl-1,4-cyclohexanedicarboxamide
10 compounds such as
  N,N'-dicyclo-hexyl-1,4-cyclohexanedicarboxamide and
  N,N'-dicyclohexyl-1,4-cyclopentanedicarboxamide.
      Examples of the diamine derivative type diamide com-
  pounds from C$_5$-C$_8$-cycloalkyl mono-carboxylic acids or C$_6$-
15 C$_{12}$-aromatic monocarboxylic acids and C$_5$-C$_8$-cycloaliphatic
  or C$_6$-C$_{12}$-aromatic diamines, optionally contained in the
  β-nucleated propylene copolymer, are
- N,N'-C$_6$-C$_{12}$-arylene-bis-benzamide compounds such as
  N,N'-p-phenylene-bis-benzamide and
20 N,N'-1,5-naphtalene-bis-benzamide,
- N,N'-C$_5$-C$_8$-cycloalkyl-bis-benzamide compounds such as
  N,N'-1,4-cyclopentane-bis-benzamide and
  N,N'-1,4-cyclohexane-bis-benzamide.
- N,N'-p-C$_6$-C$_{12}$-arylene-bis-C$_5$-C$_8$-cycloalkylcarboxamide
25 compounds such as
  N,N'-1,5-naphtalene-bis-cyclohexanecarboxamide and
  N,N'-1,4-phenylene-bis-cyclohexanecarboxamide.
- N,N'-C$_5$-C$_8$-cycloalkyl-bis-cyclohexanecarboxamide com-
  pounds such as
30 N,N'-1,4-cyclopentane-bis-cyclohexanecarboxamide and
  N,N'-1,4-cyclohexane-bis-cyclohexanecarboxamide.
      Examples of the amino derivative type diamide com-
  pounds, optionally contained in the β-nucleated propylene
  copolymer, are
35 N-phenyl-5-(N-benzoylamino)pentaneamide and/or
 N-cyclohexyl-4-(N-cyclohexylcarbonylamino)benz-amide.

Examples of the quinacridone type compounds, option-
ally contained in the β-nucleated propylene copolymer,
are quinacridone, dimethylquinacridone and/or dimethoxy-
quinacridone.

5   Examples of the quinacridonequinone type compounds,
optionally contained in the β-nucleated propylene copoly-
mer, are quinacridonequinone, a mixed crystal of 5,12-di-
hydro(2,3b)acridine-7,14-dione with quino(2,3b)acridine-
6,7,13,14-(5H,12H)-tetrone as disclosed in EP-B 0 177 961
10   and/or dimethoxyquinacridonequinone.

Examples of the dihydroquinacridone type compounds,
optionally contained in the β-nucleated propylene copoly-
mer, are dihydroquinacridone, dimethoxydihydroquinacrido-
ne and/or dibenzodihydroquinacridone.

15   Examples of the dicarboxylic acid salts of metals
from group IIa of periodic system, optionally contained
in the β-nucleated propylene copolymer, are pimelic acid
calcium salt and/or suberic acid calcium salt.

Examples of salts of metals from group IIa of perio-
20   dic system and imido acids of the formula

$$HOOC-[-CH_2-]_x-\underset{R}{CH}-N\underset{CO}{\overset{CO}{<}}Y$$
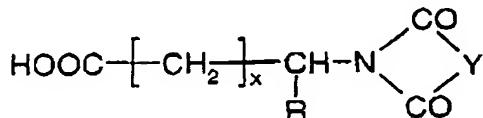
25   optionally contained in the β-nucleated propylene copoly-
mer, are the calcium salts of phtaloylglycine, hexahydro-
phtaloylglycine, N-phtaloyl-alanine and/or N-4-methyl-
phtaloylglycine.

According to the invention the β-nucleated propylene
30   polymer is mixed with microspheres, which may be made of
various organic and inorganic materials, such as glass,
epoxy resin, phenolic resin or urea-formaldehyde resin.
The microspheres should be rigid, i. e. non-compressible,
and should have a density of at most about 0.8 g/cm^3,
35   preferably at most about 0.4 g/cm^3. The outer diameter of
the microspheres should be 1-500 μm, preferably 5-200 μm
and preferably the microspheres are hollow. A preferred

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material is an inorganic glass, preferably a silica based glass, or a polymer or ceramics, a rigid foam structure, etc.

In the present invention the microspheres are pref-
5   erably untreated, i. e. they do not need any pretreatment with chain scission agent in order to achieve an even distribution of the microspheres and excellent mechanical properties. This is an advantage compared to the prior art such as EP-A-473 215 mentioned above.

10   The density of the composition of β-nucleated propy-lene polymer mixed with hollow microspheres should pre-ferably be 500-850 kg/m³ and more preferably 600-800 kg/m³.

Preferably, the microspheres are present in the com-
15   position in an amount of from 10 to 50 weight%, prefera-bly 15 to 35%, more preferably 20-30 weight% of the composition.

In order to improve the distribution of microspheres within the polymer matrix, to reduce the amount of micro-
20   spheres crushed during processing, and to improve the processability, the MFR of the β-nucleated propylene po-lymer may be increased by the incorporation into the po-lymer matrix of a polyolefin, having a MFR of 100-1500, preferably 400-1200 g/10 min at 230°C/2.16 kg. The amount
25   of polyolefin, e. g. polyethylene or polypropylene should be 0-30 weight%, preferably 10-25 weight%.

The syntactic polyolefin composition of the present invention may contain usual auxiliary materials, such as 0.01 to 2.5 wt% stabilizers and/or 0.01 to 1 wt% proces-
30   sing aids, and/or 0.1 to 1 wt% antistatic agents and/or 0.2 to 3 wt% pigments, in each case based on the polymers used.

As stabilizers, preferably mixtures of 0.01% to 0.6 wt% phenolic antioxidants, 0.01% to 0.6 wt% 3-arylbenzo-
35   furanones, 0.01% to 0.6 wt% processing stabilizers based on phosphites, 0.01% to 0.6 wt% high temperature stabili-

zers based on disulfides and thioethers and/or 0.01% to
0.8 wt% sterically hindered amines (HALS), are suitable.

5 The melt flow rate (MFR), which is equivalent to the
term "melt index" previously used, is an important pro-
perty of the syntactic polyolefin composition for pipe
coating according to the invention. The MFR is determined
according to ISO 1133 and is indicated in g/10 min. The
MFR is an indication of the flowability, and hence the
processability, of the polymer. The higher the melt flow
10 rate, the lower the viscosity of the polymer composition.
The MFR is determined at different loadings such as 2,16
kg (MFR$_2$; ISO 1133, condition D). In the present inven-
tion the composition has an MFR$_2$ in the range of 0.05-30
g/10 min at 230°C/2.16 kg, more preferably in the range
15 of 0.5-10 g/10 min at 230°C/2.16 kg and most preferably
in the range of 1.0-5 g/10 min.

Another important property of the syntactic polyole-
fin composition for pipe coating according to the inven-
tion is the elongation at break, which is determined
20 according to ISO 527-2/5A, sample thickness 2 mm, 100
mm/min, at ambient temperature of 23°C. The elongation at
break is a measure of the flexibility of the material and
consequently its ability to endure handling, such as
coiling, reeling, etc without the formation of cracks.
25 During coiling of the pipe the extension of the insulat-
ing layer may be up to about 5%, which requires a suffi-
ciently ductile material. According to the invention the
composition has an elongation at break of at least 3%,
preferably at least 5%, and more preferably at least 10%.
30 The tensile modulus is a measurement of the rigidity
of the material and its ability to withstand high water
pressures. The tensile modulus of the composition should
preferably be at least 1500 MPa determined according to
ISO 527-2/1B, sample thickness 4 mm, 1mm/min, 23 °C.
35 Another property indicating the ability of the com-
position to endure high water pressures is the compres-
sion strength determined according to ASTM D 695. At the

present invention this compression strength should pref-
erably be ≥10 MPa and more preferably ≥15 MPa.

    As previously stated the thermal conductivity of an
effective off-shore pipe insulation needs to be low in
5   order to attain the desired low level of thermal conduc-
tivity. According to the invention the composition pre-
ferably has a K-value of less than 0.20 W/m°K, preferably
less than 0.17 W/m°K.

    The present invention also relates to a method for
10   the preparation of a syntactic polyolefin composition for
pipe coating, in which hollow microspheres are evenly
distributed by melt mixing in a composition comprising a
β-nucleated propylene polymer and hollow microspheres,
said composition having a melt flow rate at 230°C/2.16kg
15   in the range of 0.05-30 g/10 min, more preferably in the
range of 0.5-10 g/10 min and most preferably in the range
of 1.0-5 g/10 min, and in that the composition has an
elongation at break of at least 3%, more preferably >5%,
and most preferably >10%.

20   The method is generally carried out in a compounding
or extruder unit, preferably in a co-rotating or counter-
rotating twin screw extruder, or in an internal mixer
such as a Banbury type mixer or in a single screw ex-
truder such as a Buss Co-kneader or in a conventional
25   single screw extruder. Static mixers such as Kenics,
Koch, etc can also be used in addition to the compounding
or extruder units mentioned in order to improve the dis-
tribution of the microspheres in the polymer matrix. Pel-
lets of β-nucleated propylene block (co)polymer and
30   optionally a propylene homopolymer are fed into the ex-
truder. When the polymer is melted the hollow micro-
spheres are added to the melted polymer, more preferably
at a melt temperature of 30°C above the melt temperature
of the polymer, most preferably 50°C above the melt tem-
35   perature of the polymer in a ratio to achieve the desired
K-value of the composition. The microspheres and polymer
are mixed in the extruder until the microspheres are

evenly distributed in the molten polymer. The molten and homogenised compound is then fed from the extruder and either pelletized for subsequent use or used directly to coat a pipe and prepare a syntactic polyolefin coated

5   pipe according to the present invention. Direct coating of the pipes is preferred and includes both the pipe coating process based on co-extrusion, i. e. coating the complete circumference at the same time or by extrusion of a tape or film wounded around the pipe in a continuous

10   process.

As indicated above the off-shore pipe coated with a syntactic polyolefin composition of the present invention is preferably prepared by extruding the syntactic poly-olefin composition of the invention, e. g. in connection

15   with the preparation thereof by melt mixing onto the pipe. Such direct coating of the pipes in a continuous process has the advantages that intermediate processing steps involving cooling, pelletizing and remelting may be omitted. In this way the tough treatments of pelletizing

20   and especially remelting in an extruder, which normally to a substantial extent is performed by friction forces, are avoided. The result of such treatments is inevitably a large amount of crushed microspheres with accompanying higher heat conductivity and loss in mechanical proper-

25   ties. The pipe may be pretreated by coating with an epoxy resin layer and an compatibilizing layer on the epoxy resin layer before the coating with the syntactic poly-olefin composition. The thickness of the coating prefer-ably is at least about 1-100 mm, more preferably 20-50

30   mm.

The present invention will now be illustrated by way of non-limiting examples of preferred embodiments in or-der to further facilitate the understanding of the inven-tion.

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Examples
Preparation of a β-nucleated propylene block copolymer.

   A mixture of 90 weight% of a propylene block copoly-
mer, obtained by combined bulk and gas phase polymeriza-
5   tion using a Ziegler-Natta catalyst system with dicyclo-
pentyldimethoxysilane as external donor, having an ethy-
lene content of 8.3 weight%, an $IR_τ$ of the propylene homo-
polymer block of 0.985 and a melt flow rate of 0.30 g/10
min at 230°C/2.16 kg, 10 weight% of a master batch comp-
10 rising 99 parts by weight of a propylene block copolymer
having an ethylene content of 8.3% by weight, an $IR_τ$ of
the propylene homopolymer block of 0.985 and a melt flow
rate of 0.30 g/10 min at 230°C/2.16 kg, and 1 part by
weight pimelic acid calcium salt, and 0.1 weight% calcium
15 stearate, 0.1 weight% tetrakis[methylene(3,5-di-t-butyl-
hydroxyhydrocinnamate)]methane and 0.1 weight% tris-(2,4-
di-t-butylphenyl)phosphite, based on the sum of the pro-
pylene polymers used, is melted in a twin screw extruder
with a temperature profile of 100/145/185/210/220/225/
20 225/225/220/200/185 °C, homogenized, discharged and pel-
letized. The resulting propylene copolymer has a melt
flow rate of 0.32 g/10 min at 230°C/2.16 kg, a tensile
modulus of 1290 MPa and a Charpy impact strength, using
notched test specimens, of 39 kJ/m^2 at -20°C.

25 Physical properties of microspheres
   The used miccrospheres were Scotchlite^{TM} Glass Bub-
bles having a density within the range of 0.35-0.41
g/cm^3, measured in accordance with ASTM D284 (1976 edi-
tion) and a bulk density in the range of 0.19-0.28 g/cm^3.
30 Isostatic test pressure evaluation, at a test pressure of
38.5 MPa, calculated from the change in density of a sam-
ple (mixed with talc) after exposure to dry nitrogen, re-
sulted in % of survival of at least 80% and typically
90%. Floatation, % by bulk volume, was typically 94%.
35 Test values were typical when material was sampled in
accordance with ASTM D2841 (1988 edition).

Example 1-3

Preparation of a composition comprising a β-nucleated propylene polymer, a propylene homopolymer and hollow microspheres.

5   Pellets of β-nucleated propylene block copolymer having a MFR of 0.3 g/10 min at 230°C/2.16 kg prepared as described above and pellets of a polypropylene homopolymer having a MFR of 400 g/10 min at 230°C/2.16 kg, were fed into the first mixer inlet of a Buss Co-Kneader 100

10   MDK/E-11L/D, i. e. a single screw mixer with a downstream discharge single screw extruder with a pelletizing unit cutting pellets in the molten stage and cooled via water. The mixer temperatures were set to 200-240°C, from first inlet to outlet, screw temperature to 210°C and the dis-

15   charge extruder to around 230°C. The mixer screw RPM was 170-190 rpm and the throughput 100-150 kg/h. Untreated microspheres, as specified above, were fed into the molten polymer in the second mixer inlet downstream. The compositions of the composite material are set forth in

20   Table 1. The composite material was extruded and pelletized.

Table 1

	Example 1 Weight%	Example 2 weight%	Example 3 Weight%
Propylene block co-polymer, MFR 0.3	58.10	48.10	
Propylene block co-polymer MFR 4.0			83.8
Homopolypropylene, MFR 450	15.00	20.00	
β-nucleator	1.2	1.2	1.2
Glass microspheres	25.00	30.00	15.00
Stabilizers	0.74	0.74	0.74

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The resulting properties from plaques compression moulded at 220°C are presented in Table 2.

Table 2

Property	Example 1	Example 2	Example 3
MFR$_2$ at 230°C/2.16kg, ISO 1133	0.55	0.9	5.4
Density, kg/m^3 ISO 1183	690	650	739
K-value, W/m°K, ASTM C177	0.174		0.188
Fraction of broken micro-spheres, %	14	8	
Tensile stress at yield, MPa, ISO 527	6	12	12
Elongation at break, % ISO 527	98	7.6	9.4
Tensile modulus, Pa, ISO 527	1900		
Compression strength at 5% compression, MPa, ASTM D695	17.8		

5   From Table 2 it can be seen that the composition
according to the invention provides a composite material
which is well suited for insulating purposes, having a K-
value of 0.174 W/m°K and a density of 650-690 kg/m^3. The
mechanical properties of the composition are excellent
10   with a high elongation at break of 98% and a tensile
modulus of 1900 MPa. The compounding of the β-nucleated
propylene polymer of MFR 0.3 g/10 min at 230°C/2.16 kg
and the propylene homopolymer of MFR 400 g/10 min at
230°C/2.16 kg results in a composition having a MFR of
15   0.55-0.9 g/10 min at 230°C/2.16 kg, and thus makes it
possible to incorporate the hollow microspheres into the
composition without any significant breakage of the
microspheres. These values correspond to the values
attained in the ready made pipe coating, wherein com-

pounding/homogenisation and pipe extrusion is performed
in a continuous step, i. e. without extrusion remelting
which causes an additional amount of crushed micro-
spheres.

5   Example 4

In order to simulate a two step procedure, wherein
melt compounding and/or homogenisation and palletising
and/or solidification is accomplished in a first step and
pipe extrusion including remelting in a subsequent second
10   step, the pellets manufactured in example 1 were extruded
in a labextruder through a tape die having a cross sec-
tion of 30x2 mm. The labextruder was a standard screw
compression screw with a RPM of 30, a screw length L/D of
30 and a screw diameter of 30 mm. The compression ratio
15   was 1:3, the set temperature 220°C, and the melt tempera-
ture 225°C. The resulting properties from plaques made of
the tapes by compression moulding at 220°C, are presented
in Table 3.

20   Table 3

Property	Example 4
MFR_2 at 230°C/2.16kg, ISO 1133	0.57
Density, kg/m^3 ISO 1183	722
K-value, $W/m°K$, ASTM C177	0.18
Fraction of broken microspheres, %	
Tensile stress at yield, MPa, ISO 527	6
Elongation at break, % ISO 527	79

From the resulting properties presented in Table 3
it can be concluded that a second extrusion step includ-
25   ing remelting by extrusion still gives suitable values

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for the application, e. g. a K-value of 0.18 W/m°K and an elongation at break of 79%.

Comparative Examples 5 and 6

Pellets of propylene block copolymer were prepared

5   as described above for examples 1-3.

Table 4

	Example 5 Weight%	Example 6 weight%
Propylene block co-polymer, MFR 1.0	70	
Propylene block co-polymer MFR 8.0	5	80
Glass microspheres	25	20

10   The resulting properties from plaques compression moulded at 220°C are presented in Table 5.

Table 5

Property	Example 5	Example 6
MFR_2 at 230°C/2.16kg, ISO 1133	0.38	2.5
Density, kg/m^3 ISO 1183	681	722
Tensile stress at yield, MPa, ISO 527	8.7	13
Elongation at break, % ISO 527	0.1	2.2

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From the resulting properties presented in Table 5 it is evident that compositions without the addition of a β-nucleating agent have inferior mechanical properties in comparison to the compositions according to the invention

20   given in examples 1-4.

CLAIMS

1. A syntactic polyolefin composition for pipe coat-ing, c h a r a c t e r i s e d in that the composition comprises a β-nucleated propylene polymer comprising a β-nucleating agent and microspheres, said composition having a melt flow rate (MFR$_2$; ISO 1133, condition D) at 230°C/2.16kg in the range of 0.05-30 g/10 min and in that the composition has an elongation at break of at least 3%.

2. A syntactic polyolefin composition according to claim 1, c h a r a c t e r i s e d in that said compo-sition has a melt flow rate (MFR$_2$; ISO 1133, condition D) at 230°C/2.16kg in the range of 0.5-10 g/10 min and pref-erably in the range of 1.0-5 g/10 min.

3. A syntactic polyolefin composition according to claim 1 or 2, c h a r a c t e r i s e d in that said composition has an elongation at break of >5% and pref-erably >10%.

4. A syntactic polyolefin composition according to any one of claims 1 to 3, c h a r a c t e r i s e d in that the β-nucleated propylene polymer is a (co)polymer which comprises at least 90.0 weight% of propylene and up to 10.0 weight% of α-olefins with 2 or 4 to 18 carbon atoms, and that the propylene polymer has a melt flow rate of 0.1-8 g/10 min at 230°C/2.16 kg.

5. A syntactic polyolefin composition according to any one of claims 1 to 4, c h a r a c t e r i s e d in that the composition further comprises a polyolefin homopolymer having a melt flow rate of 100-1500 g/10 min at 230°C/2.16 kg.

6. A syntactic polyolefin composition according to any one of claims 1 to 5, c h a r a c t e r i s e d in that the amount of polyolefin is 0-20 weight%, preferably 15-20 weight%.

7. A syntactic polyolefin composition according to any one of claims 1 to 6 , c h a r a c t e r i s e d in

that the tensile modulus of the composition is at least
1500 MPa determined according to ISO 527.

8. A syntactic polyolefin composition according to
any one of claims 1 to 7, c h a r a c t e r i s e d   in
5   that the compression strength at 20 MPa/80° determined
according to ASTM D695, is > 10 MPa, preferably >15 MPa.

9. A syntactic polyolefin composition according to
any one of claims 1 to 8, c h a r a c t e r i s e d   in
that the K-value of the composition is less than 0.190
10   W/m°K.

10. A syntactic polyolefin composition according to
any one of claims 1 to 9, c h a r a c t e r i s e d   in
that the density of the composition is 500-850 kg/m3.

11. A syntactic polyolefin composition according to
15   any of claims 1 to 10, c h a r a c t e r i s e d   in
that said microspheres are made of glass, ceramics, epoxy
resin, phenolic resin or urea-formaldehyde resin.

12. A syntactic polyolefin composition according to
any one of claims 1 to 11, c h a r a c t e r i s e d   in
20   that said microspheres are untreated microspheres.

13. A syntactic polyolefin composition according to
any one of claims 1 to 12, c h a r a c t e r i s e d   in
that said microspheres have an outer diameter of 1-500
μm, preferably 5-200 μm.

25   14. A syntactic polyolefin composition according to
any one of claims 1 to 13, c h a r a c t e r i s e d   in
that said microspheres are hollow.

15. A syntactic polyolefin composition according to
any one of claims 1 to 14, c h a r a c t e r i s e d   in
30   that said microspheres are present in an amount of 10-50
weight%, preferably 20-30 weight% of the composition.

16. A method for the preparation of a syntactic po-
lyolefin composition for pipe coating according to any
one of claims 1-15, c h a r a c t e r i s e d   in that
35   microspheres are evenly distributed by melt mixing in a
composition comprising a β-nucleated propylene polymer
and microspheres, said composition having a melt flow

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rate at 230°C/2.16kg in the range 0.05-30 g/10min and in that the composition has an elongation at break of at least 3%.

17. A method according to claim 16, c h a r a c -
5 t e r i s e d in that said microspheres are added to the molten polymer.

18. A method according to claim 16 or 17, c h a r a c t e r i s e d in that the composition is compounded/homogenised and extruded as a coating on an
10 off-shore pipe in one continuous step.

19. A method according to claim 16 or 17, c h a r a c t e r i s e d in that the composition is pelletized in a first step and in a subsequent step extruded as a coating on an off-shore pipe.

15 20. An off-shore pipe coated with a syntactic poly-olefin composition, c h a r a c t e r i s e d in that the pipe is coated with a composition according to any one of claims 1-15.

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08J 9/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08J, C08K, C08L, C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI, DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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